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The Solubility of Acid Gases in Methanol

North Carolina State Univ at Raleigh

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The Solubility of Acid Gases in Methanol

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16. ABSTRACT The report describes a thermodynamic model developed to predict phase-equilibrium behavior in a methanol/carbon-dioxide/nitrogen/hydrogen-sulfide system based on parameters determined from binary vapor/liquid equilibrium data available in the literature. Model predictions are compared with actual experimental data. Predicted values show an average deviation from experimental data of 21% for vapor compositions and 10% for total pressures, indicating the possibility of ternary effects not accounted for by the model. (The model is to be used in conjunction with a coal-gasification/gas-cleaning facility constructed at North Carolina State University as part of a study funded by the EPA. The overall objective of the project is to characterize completely the gaseous and condensed phase emissions from typical coal-gasification/gas-cleaning processes and to determine how emissions depend on process parameters. To describe and evaluate operations involved in the removal of acid gas constituents from the crude synthesis gas, information is needed concerning the equilibrium behavior of these constituents with the particular solvent used in the removal unit; hence, the model.)

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ABSTRACT

A coal gasification/gas cleaning facility has been constructed at North Carolina State University as part of a study funded by the Environmental Protection Agency. A major part of this facility involves absorption and stripping of acid gas constituents, and the description of operations to carry out these processes requires information on the equilibrium behavior of the constituents with the system's solvent. Two approaches may be used to obtain this information: measuring extensive equilibrium data or developing a thermodynamic model that uses limited data to predict equilibrium behavior. The latter approach is suggested. The system chosen for study reflects current opinion concerning the most important candidate for industrial acid gas removal systems.

A thermodynamic model was developed to predict phase equilibrium in the methanol-carbon dioxide-nitrogen-hydrogen sulfide system based on parameters determined from binary vapor-liquid equilibrium data available in the literature. An experimental apparatus for obtaining high pressure vapor-liquid equilibrium data was used to obtain data for the methanol-carbon dioxide system at -15.0°C and at pressures from 5 to 16 atmospheres. Results showed excellent agreement with published data. Equilibrium data were obtained for the methanol-carbon dioxide-nitrogen-hydrogen sulfide system at -15.0°C and pressures ranging from 8 to 35 atmospheres. Experimental liquid phase compositions and temperatures were used to predict vapor compositions and total pressures. Predicted values showed an average deviation from experimental data of 21 percent for vapor compositions and 10 percent for total pressures indicating the possibility of ternary effects not accounted for by the model.

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SECTION 1

INTRODUCTION

North Carolina State University, under the sponsorship of the Environmental Protection Agency, Industrial Environmental Research Laboratory at Research Triangle Park, is engaged in a research project to study the environmental effects of coal gasification. So that the results of this research will represent what might be expected from full-scale gasification operations, a highly flexible and complete coal gasification and gas cleaning facility has been constructed for the project. The overall objective of the project is to characterize completely the gaseous and condensed phase emissions from typical coal gasification-gas cleaning processes and to determine how emissions depend upon various process parameters.

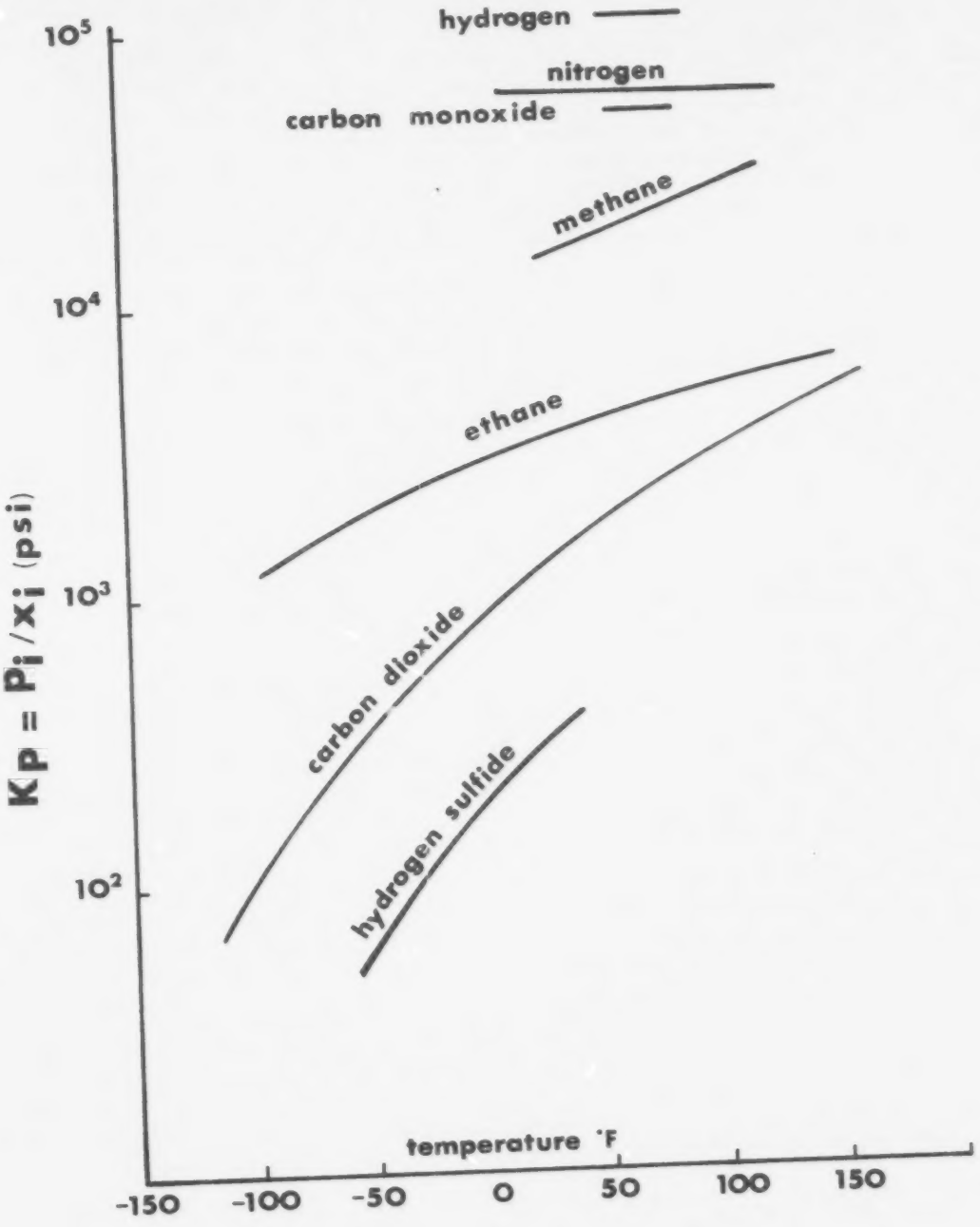
The North Carolina State University facility consists of a continuous fluidized bed gasifier, devices for removing particulates, condensables, and soluble matter from the raw synthesis gas, and an acid gas removal system (AGRS). The gasifier operates at pressures up to 100 psig, has a capacity of 50 lb coal/hr, and can run with either steam-O_2 or steam-air feed mixtures to produce roughly 25 SCFM of crude synthesis gas. The AGRS is modular in design so that alternative absorption processes may be evaluated with a minimal amount of system modification.

The primary purpose of an AGRS is to remove most of the sulfur containing compounds and, for some applications, the carbon dioxide. The processes available to accomplish this employ either chemical or physical absorption. In chemical absorption, acid gas species react with alkaline compounds or solvents; the solvent is regenerated by heating. One of the problems with processes employing chemical absorption for gas cleanup is that some of the crude gas components such as carbonyl sulfide often react with the solvents to form decomposition products which prevent complete regeneration of the solvent. Processes employing physical absorption capitalize on the differing solubilities of various gases in liquids. Polar liquids are best suited for these processes because they have a high degree of selectivity between acid gases and the valuable gas components. Methanol serves as the solvent in Lurgi's proprietary Rectisol process. It is a good solvent for hydrogen sulfide, carbonyl sulfide, carbon disulfide and carbon dioxide. As shown by plots of equilibrium constants in Figure 1, methanol will absorb hydrogen sulfide preferentially to carbon dioxide.

The economics and desirability of these two types of gas cleanup processes depend heavily on their particular application. However, the use of methanol is particularly attractive and economical for cleanup systems used in conjunction with coal gasification facilities for some applications (1). This has been demonstrated by Lurgi in their design and successful operation of the Rectisol process.

Because of its immediate importance, methanol is the first solvent that will be studied in the NCSU gas cleaning test facility and solubility data are needed to evaluate the AGRS performance.

Figure 1. Solubility of gases in methanol.



In the facility the crude gas consists mainly of nitrogen, carbon monoxide, carbon dioxide, hydrogen, ethane, water, methane, hydrogen sulfide, other sulfur gases, and small amounts of higher hydrocarbons. The gas is dehydrated, compressed to 500 psi, cooled, and fed to a packed absorber column, where it is contacted with cold methanol. Carbon dioxide, hydrogen sulfide and other sulfur gases are absorbed from the crude gas which is then discharged to a flare. Methanol enters the absorber at about -30°F. The circulating solvent flows from the bottom of the absorber through a pressure reduction valve to a flash tank at 15-25 psig. Liquid solvent leaving the flash tank is regenerated by stripping carbon dioxide and hydrogen sulfide with nitrogen.

A careful search of the literature determined that the data and correlations required for an accurate analysis of the methanol-based process are not available. Binary vapor-liquid equilibrium data for some of the system components were located, but there appears to be very little multicomponent data. It is clear that experience and proprietary data or rough estimates based on ideal solution behavior have been used in the design of existing facilities. It is not feasible to meet the requirements of the current study using either of the above approaches; without accurate vapor-liquid equilibrium data it will be almost impossible to analyze the operation of the AGRS.

It is not practical to develop an exhaustive data base for multicomponent vapor-liquid equilibrium behavior. An approach that has been used satisfactorily to describe systems similar to those encountered here is to develop a thermodynamic model that uses binary equilibrium data to predict multicomponent behavior.

The purpose of this study was to begin developing a useful model for multicomponent equilibrium behavior and to obtain binary vapor-liquid equilibrium data for systems consisting of carbon dioxide, nitrogen, hydrogen sulfide and methanol. The range of temperatures, pressures and compositions that have been considered in these studies include those found in typical acid gas removal systems. Both theoretical and experimental parts of this effort have been developed to a point that it seems appropriate to describe the progress and point out directions for future efforts. This report does that in its following sections.

SECTION 2

FUNDAMENTAL EQUATIONS

A typical composition of gases to be treated in acid gas removal systems is shown in Table 1. The nature of these components indicates that both gas and liquid solutions containing these materials will not behave ideally at the system conditions; simple thermodynamic expressions can not be used to describe their equilibrium behavior with methanol. It is necessary, therefore, either to take extensive multicomponent equilibrium data or to develop thermodynamic models using binary and perhaps

Table 1. Composition of Raw Gas from Coal Gasification (3).

Component	With O_2 (Vol. %)	With Air (Vol. %)
carbon dioxide, CO_2	31.	10.
carbon monoxide, CO	15.	19.
hydrogen, H_2	45.	22.
methane, CH_4	8.	0.5
nitrogen, N_2	0.2	48.
argon, A	0.2	...
hydrogen sulfide, H_2S	6800 ppmv	0.5
carbonyl sulfide, COS	400 ppmv	150 ppmv

limited multicomponent equilibrium data. The latter approach was used in this research.

Systems consisting of CO_2, H_2S, N_2 and methanol were chosen for study. An extensive search of the literature for equilibrium properties of binary mixtures formed by methanol and these three major acid gas components is summarized in Table 2. While some multicomponent data are available in the literature, it often is not in the range of conditions encountered in the AGRS processes or does not consider one or more of the significant components of the AGRS mixtures.

Models and Correlations

The objective of thermodynamic models and correlations is to develop expressions relating temperature, pressure and compositions in coexisting phases at equilibrium. For example, given a system pressure and a liquid phase composition, a thermodynamic model could be used to determine the system temperature and composition of a gas phase in equilibrium with the liquid. To obtain useful expressions relating these quantities it is necessary to begin with the fundamental thermodynamic relationship which states that the fugacities of a component in coexisting phase are equal at equilibrium; for vapor-liquid equilibrium

$$f_i^L = f_i^V \tag{1}$$

Two methods can be used to express these fugacities in terms of system temperature, pressure and composition of each phase. The first follows from an exact thermodynamic treatment of the system to give either of the following equations:

$$\ln f_i = \frac{1}{RT} \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_{j\neq i}} - \frac{RT}{V}\right] dV - \ln \frac{V}{n_i RT} \tag{2}$$

$$\ln f_i = \frac{1}{RT} \int_0^P \left[\left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq i}} - \frac{RT}{P}\right] dP + \ln y_i P \tag{3}$$

To use Equation 2 a pressure explicit equation of state must be available and it must describe the system over the limits of the integration. Equation 3 requires a volume explicit equation of state. This technique can be and is used to estimate gas phase fugacities but, since no single equation of state can be used to describe a mixture from ideal gas conditions to liquid conditions at elevated pressures, a second approach is used to estimate liquid fugacities.

Liquid fugacities may be defined in terms of their deviation from ideal solution behavior, as given by Raoult's or Henry's laws. The working equation is

Table 2. Binary equilibrium data from literature

Binary	Pressure Range, Atm	Temperature Range, °C	Source
CO_2 - CH_3OH	2,33	0,-30	Yorizane et al (4)
CO_2 - CH_3OH	1,30	185,-50	Bezdel and Teodorovich (5)
CO_2 - CH_3OH	16,43	60,15	Hemmaplardh and King (6)
CO_2 - CH_3OH	2,60	25	Katayama et al (7)
CO_2 - CH_3OH	7,69	0,75	Krichevakii and Lebedova (8)
CO_2 - CH_3OH	5,80	40,25	Ohgaki and Katayama (9)
N_2 - CH_3OH	35,63	60,15	Hemmaplardh and King (6)
H_2S - CH_2OH	2,10	0,-25	Yorizane et al (4)
H_2S - CH_3OH	1	30,-30	Bezdel and Teodorvich (5)
CO_2 - H_2S	10,89	89,0	Bierlein and Kay (10)
CO_2 - H_2S	7,82	91,-48	Sobocinski and Kurata (11)
N_2 - H_2S	3,136	-45,-73	Kalra, Krishman and Robinson (12)
N_2 - H_2S	11,204	71,-17	Besserer and Robinson (13)
N_2 - CO_2	24,143	15,-20	Arai, Kaminish and Saito (14)
N_2 - CO_2	37,125	25,-40	Kaminishi and Toriumi (15)

$$f_i^L = \gamma_i (f_i^L)_{ideal} = \gamma_i \, x_i \, f_i^o \qquad (4)$$

where γ_i defines the deviation of the solution from ideal behavior and f_i^o is the fugacity of the reference state at the system conditions. If the ideal solution is defined in terms of Raoult's law then

$$f_i^o = (f_i^L)_{pure} = P_i^* \, (T) \, \phi_i^* \, (T) \exp \left[\int_{P_i^*}^{P} \frac{v_i^L (T,P) \, dP}{RT} \right] \qquad (5)$$

When this definition of the reference state is used

$$\gamma_i \to 1.0 \quad \text{as} \quad x_i \to 1.0.$$

A major difficulty associated with using the Raoult's law definition of the ideal state is evaluating P_i^* for components having a critical temperature below the system temperature. In this case a hypothetical value of the vapor pressure can be estimated by extrapolation of P_i^* vs. T expressions.

When the ideal solution is defined in terms of Henry's law

$$f_i^o = (f_i^L)_{inf} = H_i \text{ (Henry's constant)} \qquad (6)$$

Using this definition of the reference state $\gamma_i \to 1.0$ as $x_i \to 0$. O'Connell (16) has noted severe difficulties in using Henry's law to define the reference state for multicomponent systems. Therefore, Raoult's law has been used in this research.

Although significant progress has been made in developing techniques to predict activity coefficients from solution theory, it is almost always necessary to rely on experimental data for the development of suitable correlative and predictive routines. The van Laar, Margules, Wilson (17) and UNIQUAC (18) equations have been used with varying degrees of success to correlate activity coefficients. In most cases fairly accurate predictions of multicomponent system behavior can be obtained by using parameters evaluated by fitting these equations to data for each binary mixture making up the system.

SECTION 3

MODEL DEVELOPMENT

The primary constituents of methanol-based acid gas removal systems are CO_2, H_2S, N_2 and methanol. A description of the phase equilibrium behavior of quaternary mixtures of these components is necessary for a quantitative analysis of absorber and stripper operations in these processes.

The initial approach in this investigation was patterned after that reportedly used industrially for process development and design studies with high pressure nonideal systems (19). A modified Redlich-Kwong equation was used to calculate fugacities of the gaseous components, the four suffix Margules form of the Wohl equation was used to correlate activity coefficients, and the Chao-Seader equation (20) was used to estimate the fugacity of the reference state (pure liquid at the system conditions).

The Wohl equation gives the activity coefficient of a component in a multicomponent solution as

$$\ln \gamma_i = 4 \sum_{j=1} \sum_{k=1} \sum_{\ell=1} x_j x_k x_\ell \beta_{ijk\ell} - \sum_{i=1} \sum_{j=1} \sum_{k=1} \sum_{\ell=1} x_i x_j x_k x_\ell \beta_{ijk\ell} \quad (7)$$

where the values of $\beta_{ijk\ell}$ are related to binary Margules constants and a ternary constant; the Margules constants are defined for a binary mixture by the expression

$$\ln \gamma_i = x_j^2 [A_{ij} + 2(A_{ji} - A_{ij} - D_{ij}) x_i + 3D_{ij} x_i^2] \quad (8)$$

Table 3 gives the definition of $\beta_{ijk\ell}$ in terms of the binary Margules constants. Following the observation of Adler, Friend and Pigford (21), the ternary constants C^*_{ijk} were set equal to zero. Nonlinear least squares techniques can be used to estimate the Margules constants in Equation 8. Adler, Ozkardesh and Schreiner (22) showed that the temperature dependence of these parameters follow either a directly proportional or inversely proportional relationship with temperature.

The Redlich-Kwong equation of state as modified by Prausnitz and Chueh (23) was used with Equation 2 to estimate vapor phase fugacity coefficients. This equation of state is described in the following relationships.

$$P = \frac{RT}{V-b} - \frac{a}{T^{0.5} V(V+b)} \quad (9)$$

Table 3. Relationships of binary Margules parameters to multicomponent parameters.

Combination	$\beta_{ijk\ell}$
$i = j = k = \ell$	0
$i = j = \ell \neq k$	$A_{ki}/4$
$i = \ell \neq j = k$	$(A_{ij} + A_{ji} - D_{ij})/6$
$j = \ell \neq k \neq i$	$[(A_{kj} + A_{ij} + A_{jki}) - C^*_{ijk}]/12$
$i \neq j \neq k \neq \ell$	$(A_{ijk} + A_{ik\ell} + A_{jk\ell})/24$

where

$$2A_{ik\ell} = A_{ik} + A_{ki} + A_{i\ell} + A_{\ell i} + A_{k\ell} + A_{\ell k}$$

C^*_{ijk} = ternary constant

$$b = \sum_{i=1}^{n} y_i b_i \tag{9a}$$

$$b_i = \frac{\Omega_{b_i} R T_{c_i}}{P_{c_i}} \tag{9b}$$

$$a = \sum_{i=1}^{n} \sum_{j=1}^{n} y_i y_j a_{ij} \tag{9c}$$

$$a_{ii} = \frac{\Omega_{a_i} R^2 T_{c_i}^{2.5}}{P_{c_i}} \tag{9d}$$

$$a_{ij} = \frac{(\Omega_{a_i} + \Omega_{a_j}) R^2 T_{c_{ij}}^{2.5}}{2P_{c_{ij}}} \qquad (9e)$$

$$T_{c_{ij}} = \sqrt{T_{c_i} T_{c_j}} (1 - k_{ij}) \qquad (9f)$$

$$P_{c_{ij}} = \frac{4T_{c_{ij}} \left(\frac{P_{c_i} V_{c_i}}{T_{c_i}} + \frac{P_{c_j} V_{c_j}}{T_{c_j}}\right)}{(V_{c_j}^{1/3} + V_{c_j}^{1/3})^3} \qquad (9g)$$

All of the mixing rules were taken from Prausnitz (24) except (9g) which came from Tarakad and Darmer (25). The binary constant, k_{ij}, is independent of composition, temperature and density. Table 4 lists the values k_{ij} used in this study and their sources. The dimensionless pure component constants are characteristic of a particular substance and are calculated from volumetric data for the pure saturated vapor. All pure component parameters used are listed in Table 5.

An expression for the vapor phase fugacity coefficient of a component in a mixture of n components is obtained by combining Equations 2 and 9.

Table 4. Binary interaction constants for Redlich-Kwong equation

System	k_{ij}	Source
$CH_3OH - CO_2$	0.063	(25)
$CH_3OH - H_2S$	0.14	(25)
$CH_3OH - N_2$	0.14	(25)
$CO_2 - H_2S$	0.08	(24)
$CO_2 - N_2$	0.048	(25)
$H_2S - N_2$	0.105	(12)

Table 5. Pure component parameters

Component	Ω_a †	Ω_b †	T_c* (°K)	P_c* (atm)	V_c* (cc/mole)	ω*
CH_3OH	0.8451	0.2075	512.6	79.9	118.0	0.559
CO_2	0.4470	0.0911	304.2	72.8	94.0	0.225
H_2S	0.4340	0.0882	373.2	88.2	98.5	0.100
N_2	0.4290	0.0870	126.2	33.5	87.5	0.040

†From Prausnitz (24) except values for methanol which were calculated from volumetric data of Eubank (27).

*From Reid, et al. (26).

$$\ln \phi_K = \ln \frac{V}{V-b} + \frac{b_k}{V-b} - \frac{2 \sum_{i=1}^{n} y_i a_{ik}}{RT^{1.5} b} \ln \frac{V+b}{b} \qquad (10)$$

$$+ \frac{a\, b_k}{RT^{1.5} b^2} \left[\ln \frac{V+b}{V} - \frac{b}{V+b}\right] - \ln \frac{PV}{RT}$$

The molar volume of the mixture, V, is found by solving Equation 9 for the largest real root.

Various equations were used to calculate the fugacities of the reference state, chosen to be the pure liquid. The exact thermodynamic relationship given in Equation 5 was used for methanol. The vapor pressure for methanol was calculated from the Antoine equation.

$$\log [P^*(\text{mm Hg})] = 7.87862 - 1473.11/[T(°K) - 43.247] \qquad (11)$$

The Antoine constants used were determined from experimental vapor pressure data from Eubank (27) for temperatures from -40°C to +30°C. The molar volume of methanol was calculated from a corresponding states correlation of Chueh and Prausnitz (Reid, Prausnitz and Sherwood (26)).

$$1/V_i^L = \rho = \rho_s[1 + \frac{9Z_c N(P-P^*)}{P_c}]^{1/9} \quad (12)$$

$$N = (1.0 - 0.89\omega)[\exp(6.9547 - 76.2853\ T_r + 191.3060\ T_r^2 - 203.5472\ T_r^3 + 82.8731\ T_r^4)] \quad (12a)$$

$$\rho_s = \rho_c/(V_r^{(0)} + \omega V_r^{(1)} + \omega^2 V_r^{(2)}) \quad (12b)$$

$$\rho_c = 1/V_c \quad (12c)$$

$$V_r^{(j)} = a_j + b_j\ T_r + c_j\ T_r^2 + d_j\ T_r^3 + e_j/T_r + f_j\ \ln(1-T_r) \quad (12d)$$

The constants for Equation (12d) are given in Table 6. Using the above correlation for liquid molar volume and evaluating the integral in Equation 5, the following expression is obtained for the pure liquid reference fugacity.

$$f_i^o = P_i^*\ \phi_i^*\ \exp\left(\frac{P_{c_i}}{8RT\ \rho_{s_i} Z_{c_i}}\left[\left(1 + \frac{9Z_{c_i} N(P-P_i^*)}{P_{c_i}}\right)^{8/9} - 1\right]\right) \quad (13)$$

For carbon dioxide and hydrogen sulfide, a three parameter reduced states correlation was used (28)

$$\log \frac{f_i^o}{P} = \log \nu^{(0)} + \omega \log \nu^{(1)} \quad (14)$$

$$\log \nu^{(0)} = B_0 + B_1\ P_r + B_2\ P_r^2 - \log P_r \quad (14a)$$

$$B_0 = -20.651608 + 84.517272\ T_r - 15.376424\ T_r^2 + 152.65216\ T_r^3 - 84.899391\ T_r^4 + 24.84688\ T_r^5 - 2.9786581\ T_r^6 \quad (14b)$$

If $0.8 > T_r \geq 0.3$, $B_1 = \left(\frac{0.293}{2.303\ T_r}\right)[1+(1-T_r)^{0.286}]$ (14c)

If $0.9 > T_r \geq 0.8$, $B_1 = 0.321895\ T_r - 0.184316$

If $1.8 \geq T_r > 0.9$, $B_1 = 58.16962 - 326.54444\ T_r$

$+ 775.11716\ T_r^2 - 1006.8122\ T_r^3 + 773.32667\ T_r^4 - 351.56938\ T_r^5$

$+ 87.677429\ T_r^6 - 9.2617986\ T_r^7$

Table 6. Constants for equation (12')

j	a_j	b_j	c_j	d_j	e_j	f_j
0	0.11917	0.009513	0.21091	-0.06922	0.07480	-0.084476
1	0.98465	-1.60378	1.82484	-0.61432	-0.34546	0.087037
2	-0.55314	-0.15793	-1.01601	0.34095	0.46795	-0.239938

If $0.8 > T_r \geq 0.3$, $B_2 = 0$

If $0.9 > T_r \geq 0.8$, $B_2 = 0.0549369\ (0.8 - T_r)$

If $1.0 > T_r \geq 0.9$, $B_2 = 0.673344 \times 10^{-3} - 0.685226 \times 10^{-2}\ T_r$ (14d)

If $T_r \geq 1.0$, $B_2 = 0.72203901 - 2.7182597\ T_r + 3.984423\ T_r^2$

$- 2.8712448\ T_r^3 + 1.0202739\ T_r^4 - 0.14314712\ T_r^5$

$\log \nu^{(1)} = \log \nu_{0.6}^{(1)} + (P_r - 0.6)\left(\frac{\partial \log \nu^{(1)}}{\partial P_r}\right)$ (14e)

$$\log \nu_{0.6}^{(1)} = -660.08698 + 7766.7774\, T_r - 40007.379\, T_r^2 + 116582.6\, T_r^3 - 209756.24\, T_r^4 + 238673.14\, T_r^5 - 167856.45\, T_r^6 + 66762.602\, T_r^7 - 11504.984\, T_r^8 \qquad (14f)$$

$$\frac{\partial \log \nu^{(1)}}{\partial P_r} = -0.28997623 + 0.96418856\, T_r - 1.3344703\, T_r^2 + 0.82575807\, T_r^3 - 0.18939410\, T_r^4 \qquad (14g)$$

For nitrogen, the Chao-Seader equation with adjusted parameters was used (29).

$$\log \frac{f_i^o}{P} = 2.7365534 - 1.9818310/T_r - 0.51487289\, T_r + 0.042470988\, T_r^2 - 0.002814385\, T_r^3 + (-0.029474696 + 0.021495843\, T_r)\, P_r - \log P_r + \omega_i \qquad (15)$$

To use the techniques described, activity coefficients were evaluated from literature x-y-P-T data on the six possible binary mixtures of the four component system: methanol-CO_2, methanol-H_2S, methanol-N_2, CO_2- H_2S, CO_2-N_2, and H_2S-N_2. Using the references listed in Table 3, Margules parameters and their temperature dependence were determined using a non-linear least squares procedure as described by Bass (30). The results of these evaluations are summarized in Table 7 and discussed in the following paragraphs. Details of computer programs are given by Bass (30).

Table 7. Margules parameters

Binary	T_1 (°K)	A_{ij}	A_{ji}	D_{ij}	Temperature dependence
$CH_3OH - CO_2$	298.2	1.1672	0.5940	0.5056	$A'' = A' T_1/T_2$
$CH_3OH - H_2S$	258.2	1.0694	0.6608	1.0068	$A'' = A' T_1/T_2$
$CO_2 - H_2S$	293.2	0.6607	0.5141	0.5991	$A'' = A' T_2/T_1$
$CO_2 - N_2$	253.3	1.2832	0.4359	2.5135	$A'' = A' T_1/T_2$
$H_2S - N_2$	300.1	0.6165	0.7885	-0.1280	$A'' = A' (T_1/T_2)^{-1.7}$
					$D'' = D' (T_2/T_1)^{-1.7}$
$CH_3OH - N_2$	298.2	0.6317	0.7683	1.6583	$A'' = A' T_1/T_2$
					$D'' = D' T_2/T_1$

Model parameters for the methanol-carbon dioxide system were determined from the 298°K data of Katayama et al. (7). The model fit is illustrated in Table 8. Predictions are compared with the 258°K and 243°K data of Yorizane et al. (4) in Tables 9 and 10. Vapor phase compositions at the latter two temperatures were not available for comparison. Average deviations of the predicted equilibrium pressure from measured values increase with further extrapolations from 298°K but plots of the model (Figure 2) appear to be asymptotic to the experimental values at higher concentrations.

Model parameters for the methanol-hydrogen sulfide system were determined from the 258°K data of Yorizane et al. (4); the fit is shown in Table 11. Vapor compositions were not given and the concentration of methanol was reported to be too low to be measured. For the purposes of determining activity coefficients, the vapor composition of methanol was assumed to be 0.0001. Extrapolations to 273°K and 248°K show an excellent fit to the experimental data except for high hydrogen sulfide concentrations at 273°K where the assumed vapor composition is expected to be most in error. Figure 3 graphically compares the model to Yorizane's data.

Figure 2. P-x Diagram for $CH_3OH(1)$-$CO_2(2)$.

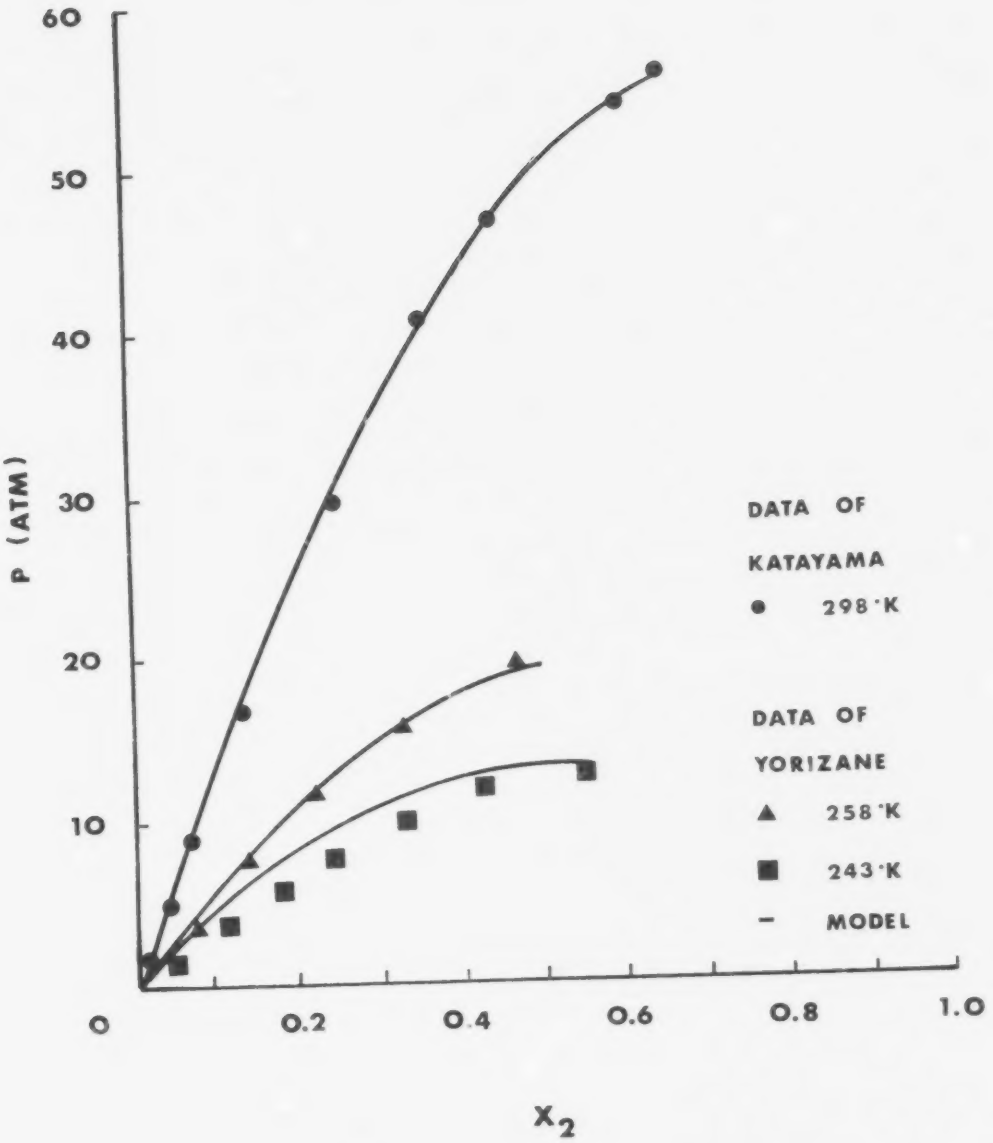


Table 11. Calculated and experimental equilibrium data for methanol-hydrogen sulfide at 258°K.

x_2	P_{exp} (atm)	P_{calc} (atm)	DP (atm)
0.165	2.0	2.4	0.4
0.231	3.0	3.0	0
0.298	3.4	3.5	0.1
0.367	4.2	4.0	0.2
0.403	4.4	4.4	0
0.490	5.0	5.0	0
0.585	5.4	5.5	0.1
0.662	5.8	5.8	0

Average percent deviation in P = 3.7.

Table 12. Calculated and experimental equilibrium data for methanol-hydrogen sulfide at 248°K.

x_2	P_{exp} (atm)	P_{calc} (atm)	DP (atm)
0.203	2.0	2.1	0.1
0.290	2.5	2.6	0.1
0.327	3.0	2.8	-0.2
0.465	3.4	3.5	0.1
0.582	4.0	4.0	0
0.733	4.3	4.3	0

Average percent deviation in P = 31.

Figure 3. P-x Diagram $CH_3OH(1)$-$H_2S(2)$.

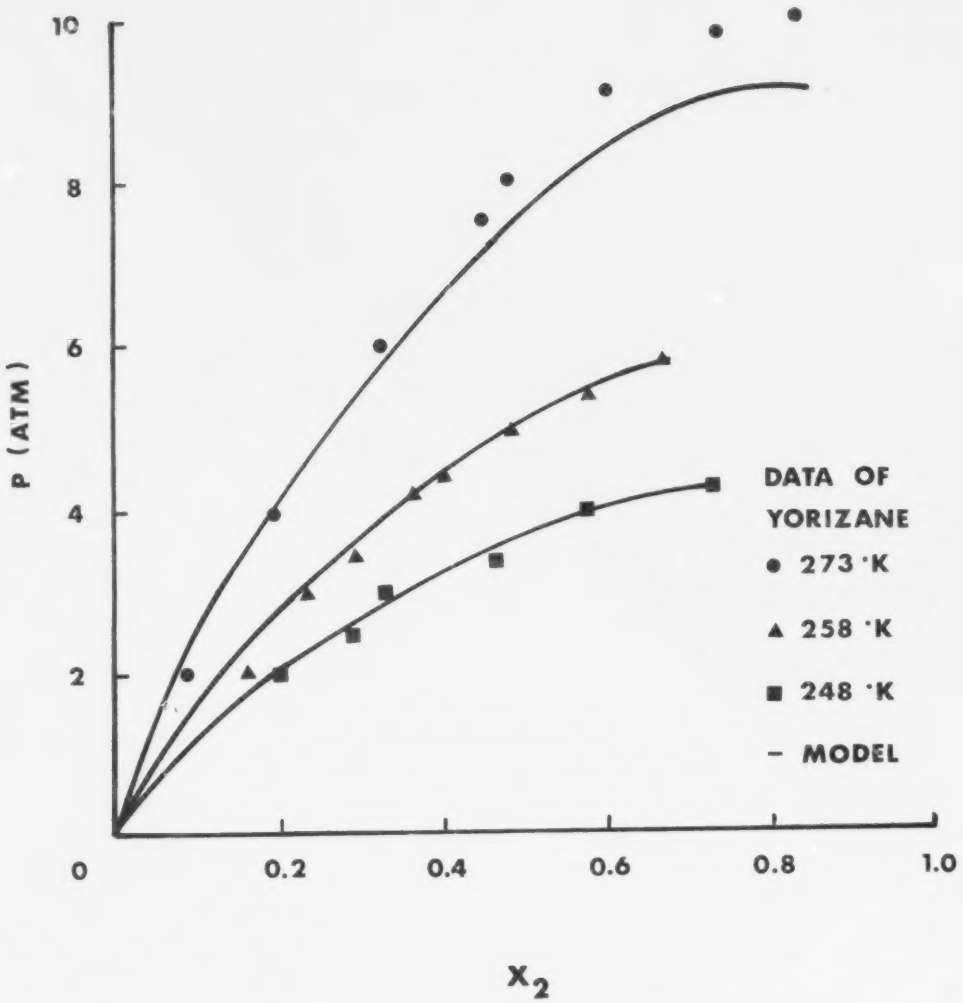


Table 13. Calculated and experimental equilibrium data for methanol-hydrogen sulfide at 273°K.

x_2	P_{exp} (atm)	P_{calc} (atm)	DP (atm)
0.092	2.0	2.4	0.4
0.199	4.0	4.0	0
0.329	6.0	5.6	-0.4
0.453	7.5	7.1	-0.4
0.484	8.0	7.4	-0.6
0.608	9.1	8.5	-0.6
0.743	9.8	9.0	-0.8
0.840	10.0	9.2	-0.8

Average percent deviation in P = 7.8.

High pressure vapor-liquid equilibrium data for the methanol-nitrogen system are scarce. Model parameters for this system were determined from the 298°K data of Hemmaplardh and King (6) with the fit illustrated in Table 14. As shown in Table 15 extrapolations to 310°K produced good agreement between predicted and experimental vapor phase compositions but poor agreement between predicted and experimental pressures. Figure 4 shows how the model fits both sets of data. More data are needed before an improved fit can be obtained. However, the region of primary interest is for pressures at or below 35 atmospheres where the model predictions are expected to be more accurate.

Model parameters for the carbon dioxide-hydrogen sulfide system were determined from the 293°K data of Bierlein and Kay (10); the resulting fit is illustrated in Table 16. Extrapolations were made to 277.6°K for comparison with data from Sobocinski and Kurata (11) with the resulting fit shown in Table 17 and Figure 5.

Table 14. Calculated and experimental equilibrium data for methanol-nitrogen at 298°K.

x_2	P_{exp} (atm)	P_{calc} (atm)	DP (atm)	$y_{2_{exp}}$	$y_{2_{calc}}$	Dy
0.0241	35.8	32.3	-3.5	0.9939	0.9941	0.0002
0.0295	35.1	37.7	2.6	0.9938	0.9934	-0.0004
0.0483	49.8	52.8	3.0	0.9952	0.9954	0.0002
0.0575	62.8	58.4	-4.4	0.9958	0.9957	-0.0001

Average percent deviation: in P, 7.6; in y, 0.02.

Table 15. Calculated and experimental equilibrium data for methanol-nitrogen at 310°K.

x_2	P_{exp} (atm)	P_{calc} (atm)	DP (atm)	$y_{2_{exp}}$	$y_{2_{calc}}$	Dy
0.0355	35.0	40.0	5.0	0.9891	0.9902	0.0011
0.0539	43.7	52.1	8.4	0.9909	0.9919	0.0010
0.0559	47.7	53.2	5.5	0.9914	0.9921	0.0007
0.0611	48.6	55.8	7.2	0.9915	0.9923	0.0008

Average percent deviation: in P, 15; in y, 0.09.

Table 16. Calculated and experimental equilibrium data for carbon dioxide-hydrogen sulfide at 293°K.

x_2	exp (atm)	calc (atm)	DP (atm)	$y_{2_{exp}}$	$y_{2_{calc}}$	Dy
0.980	20.0	19.4	-0.6	0.869	0.851	-0.018
0.910	25.0	26.4	1.4	0.685	0.633	-0.052
0.821	30.0	31.1	1.1	0.550	0.533	-0.017
0.715	35.0	34.7	-0.3	0.457	0.462	0.005
0.580	40.0	38.9	-1.1	0.370	0.381	0.011
0.437	45.0	43.4	-1.6	0.290	0.293	0.003
0.261	50.0	48.2	-1.8	0.189	0.192	0.003
0.180	52.0	49.7	-2.3	0.130	0.147	0.017

Average percent deviation: in P, 3.4; in y, 4.1.

Figure 4. P-x Diagram for $CH_3OH(1)$-$N_2(2)$.

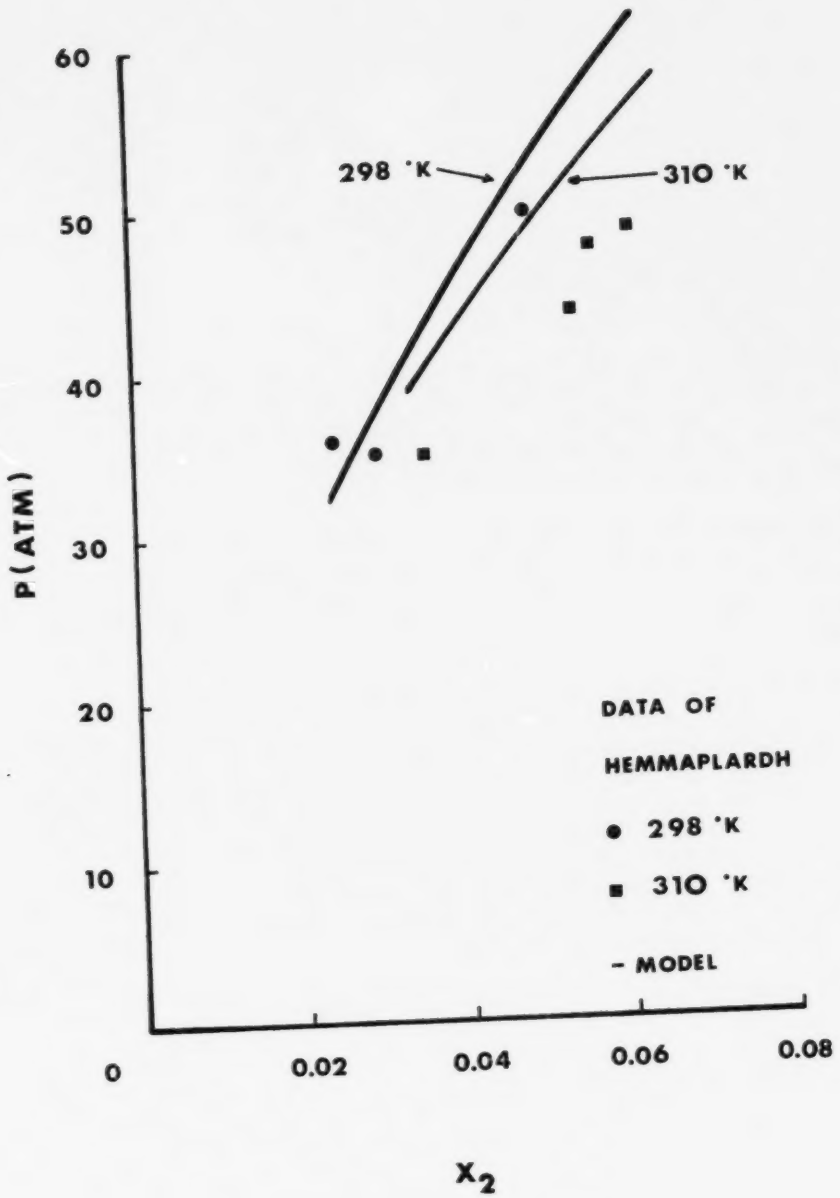


Table 17. Calculated and experimental equilibrium data for carbon dioxide-hydrogen sulfide at 277.6°K.

x_2	P_{exp} (atm)	P_{calc} (atm)	DP (atm)	$y_{2_{exp}}$	$y_{2_{calc}}$	Dy
0.967	13.61	14.60	0.99	0.855	0.774	-0.081
0.915	17.0	18.14	1.14	0.660	0.621	-0.039
0.850	20.41	20.88	0.47	0.540	0.532	-0.008
0.757	23.0	23.50	0.50	0.470	0.458	-0.012
0.605	27.22	27.07	-0.15	0.355	0.363	0.008
0.485	30.0	29.89	-0.11	0.214	0.292	0.078
0.340	33.0	33.15	0.15	0.210	0.210	0
0.290	34.02	34.15	0.13	0.185	0.184	-0.001

Average percent deviation: in P, 2.5; in y, 7.3.

Model parameters for the carbon dioxide-nitrogen system were determined from the 253°K data of Kaminishi and Toriumi (15). Extrapolations to 273°K were compared to data from the same source. These results are shown in Tables 18 and 19 and in Figure 6. The best fit was obtained at pressures below 80 atmospheres.

Model parameters for the hydrogen sulfide-nitrogen system were determined from the 300.1°K data of Besserer and Robinson (13). Extrapolation to 277.7°K was fit best by having the Margules constants proportional to temperature to the 1.7 power. The resulting fits are shown in Tables 20 and 21 and Figure 7.

Poor fits were observed for both the methanol-nitrogen and carbon dioxide-nitrogen systems. Data were not available over a wide concentration range for either system. For instance, in the carbon dioxide-nitrogen system, data at low nitrogen concentrations allowed an accurate determination of A_{21} but the lack of data at low carbon dioxide concentrations prevented an accurate determination of A_{12}. Thus, the model fits the experimental data more closely at low nitrogen concentrations and consequently at low pressures. This problem was even more pronounced in the methanol-nitrogen system where the data were even more limited and had significant scatter.

Good fits were obtained for the methanol-carbon dioxide, methanol-hydrogen sulfide and carbon dioxide-hydrogen sulfide systems. Among these three systems, the average percent deviation in pressure was 6.6 and in vapor phase composition was 2.3. In the absence of ternary effects, it is reasonable to assume that the model will provide a good estimate of total pressure and vapor phase composition for a mixture consisting of these three components. Predictions for the four component system containing nitrogen is expected to be less reliable.

Figure 5. P-x Diagram for $CO_2(1)$-$H_2S(2)$.

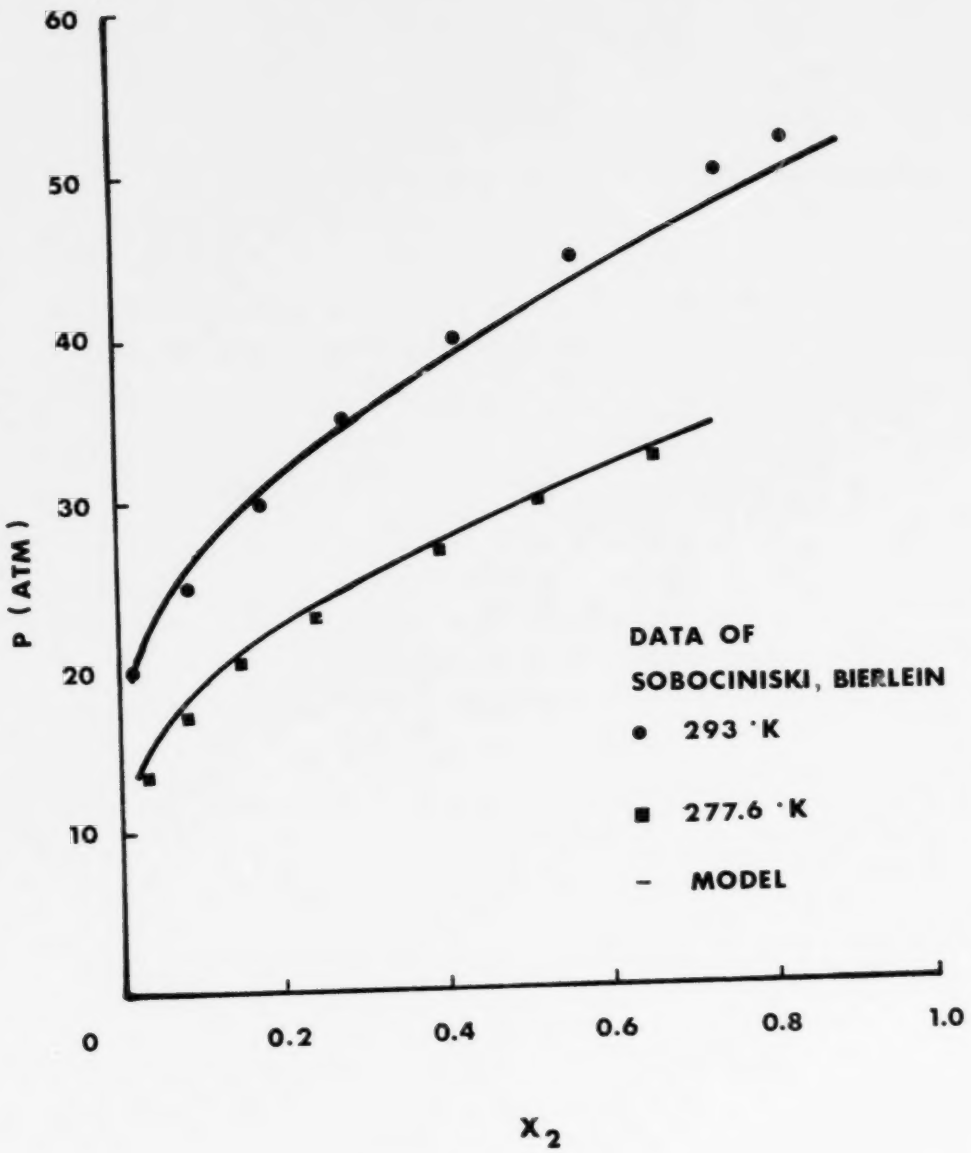


Table 18. Calculated and experimental equilibrium data for carbon-dioxide-nitrogen at 253°K.

x_2	P_{exp} (atm)	P_{calc} (atm)	DP (atm)	$y_{2_{exp}}$	$y_{2_{calc}}$	Dy
0.023	36.5	33.7	-2.8	0.382	0.411	-0.029
0.059	52.0	51.1	-0.9	0.509	0.555	0.046
0.095	67.5	63.5	-4.0	0.568	0.609	0.041
0.170	100.5	86.5	-14.0	0.596	0.668	0.072
0.210	115.8	101.2	-14.6	0.582	0.692	0.110
0.246	125.7	117.2	-8.5	0.557	0.713	0.156

Average percent deviation: in P, 8.1; in y, 14.

Table 19. Calculated and experimental equilibrium data for carbon-dioxide-nitrogen at 273°K.

x_2	P_{exp} (atm)	P_{calc} (atm)	DP (atm)	$y_{2_{exp}}$	$y_{2_{calc}}$	Dy
0.076	73.2	77.9	4.7	0.353	0.400	0.047
0.133	95.0	100.3	5.3	0.395	0.444	0.049
0.188	108.7	122.8	14.1	0.377	0.471	0.094
0.215	112.3	135.5	23.2	0.366	0.487	0.121

Average percent deviation: in P, 11; in y, 21.

Figure 6. P-x Diagram for $CO_2(1)$-$N_2(2)$.

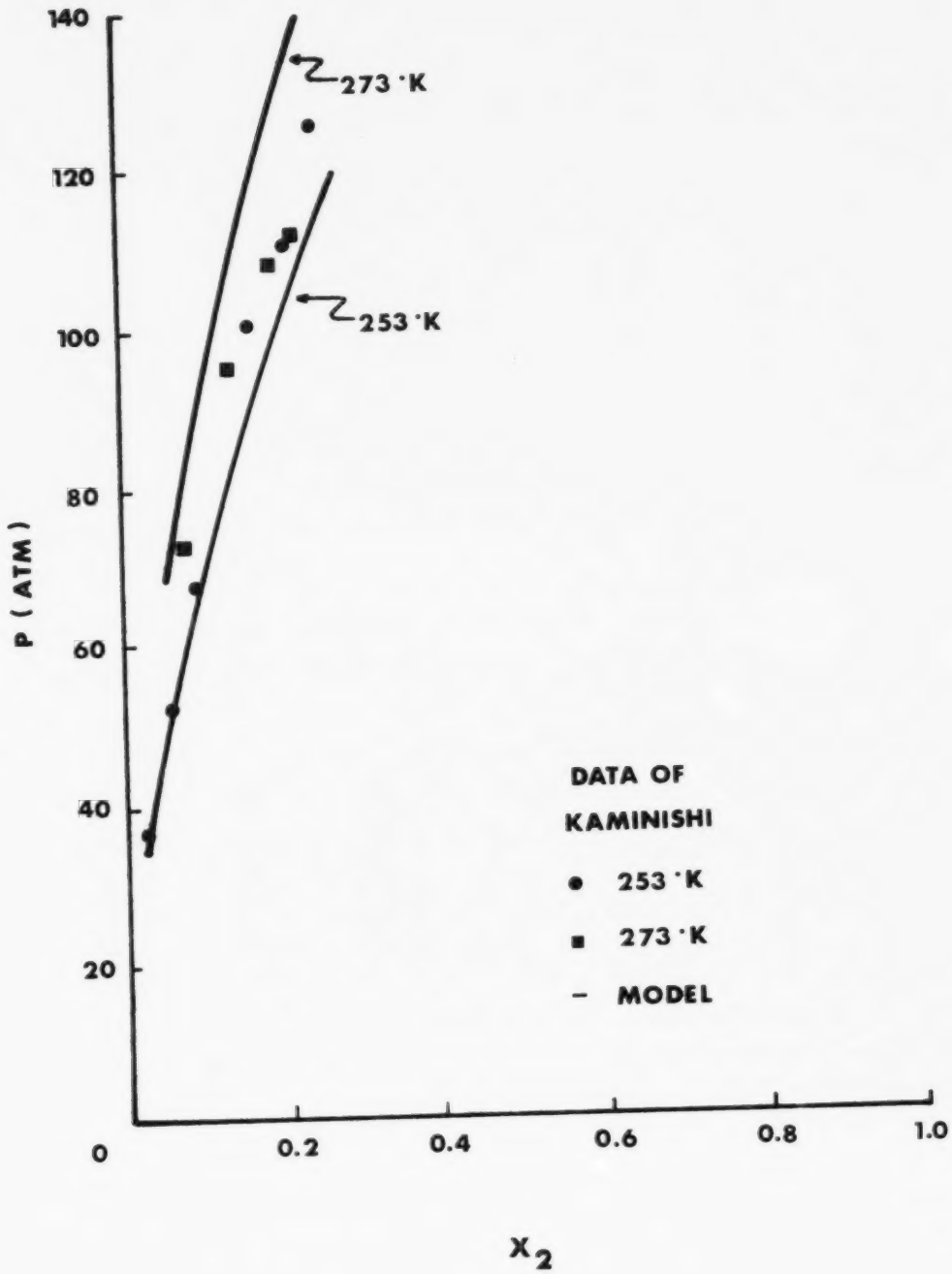


Table 20. Calculated and experimental equilibrium data for hydrogen sulfide-nitrogen at 300.1°K.

x_2	P_{exp} (atm)	P_{calc} (atm)	DP (atm)	$y_{2_{exp}}$	$y_{2_{calc}}$	Dy
0.0071	34.7	33.3	-1.4	0.332	0.352	0.020
0.0153	50.7	49.6	-1.1	0.488	0.514	0.026
0.0239	69.1	66.7	-2.4	0.576	0.598	0.022
0.0317	86.1	82.1	-4.0	0.628	0.642	0.014
0.0401	101.9	98.8	-3.1	0.653	0.672	0.019
0.0495	119.0	117.3	-1.7	0.674	0.692	0.018
0.0570	135.7	131.9	-3.8	0.684	0.703	0.019
0.0663	152.9	149.9	-3.0	0.691	0.711	0.020
0.0762	170.7	168.7	-2.0	0.695	0.716	0.025
0.0844	187.2	183.9	-3.3	0.694	0.719	0.025
0.0957	204.1	204.4	0.3	0.693	0.720	0.027

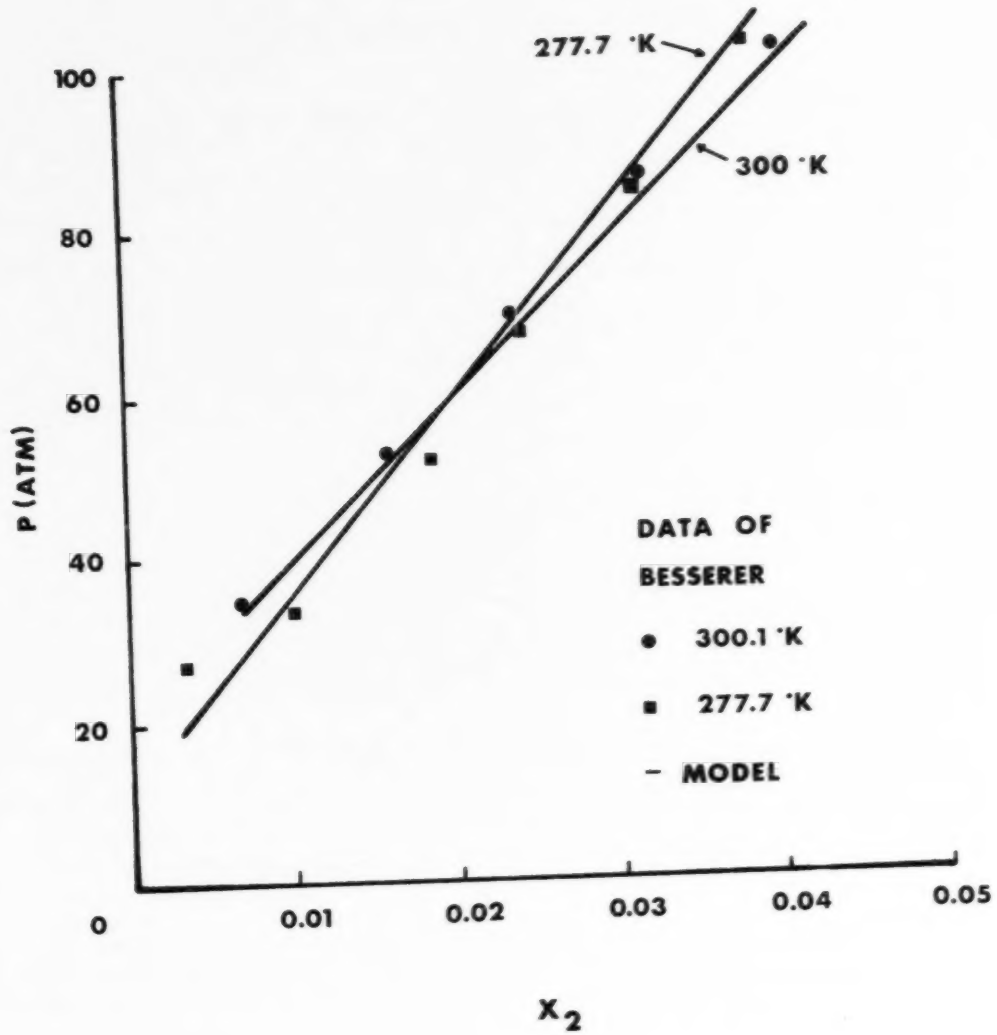
Average percent deviation: in P, 2.4; in y, 3.6.

Table 21. Calculated and experimental equilibrium data for hydrogen sulfide-nitrogen at 277.7.

x_2	P_{exp} (atm)	P_{calc} (atm)	DP (atm)	$y_{2_{exp}}$	$y_{2_{calc}}$	Dy
0.0035	17.1	19.7	2.6	0.271	0.383	0.112
0.0102	33.7	35.7	2.0	0.582	0.622	0.040
0.0186	52.1	55.9	3.8	0.698	0.726	0.028
0.0241	67.4	69.0	1.6	0.743	0.760	0.017
0.0314	85.1	86.2	1.1	0.769	0.788	0.019
0.0377	102.1	101.0	-1.1	0.791	0.804	0.013

Average percent deviation: in P, 5.5; in y, 9.8.

Figure 7. P-x Diagram for $H_2S(1)$-$N_2(2)$.



It is difficult to estimate the error involved as it was not possible to test the binary predictions for all of the nitrogen containing systems in the concentration and pressure range of interest.

To test predictions of the equilibrium behavior of CO_2-H_2S-N_2- methanol mixtures it was necessary to obtain x-y-P-T data experimentally. The apparatus and procedures used to do this are described in the following section. Results of the experimental study are discussed in Section 5.

SECTION 4

EXPERIMENTAL EQUIPMENT AND PROCEDURE

The experimental apparatus used in obtaining high pressure vapor liquid equilibrium data is shown in Figure 8. The stainless steel 565-ml equilibrium cell was equipped with baffles and agitated with a magnetic stirrer. Pressures were measured using a 16 inch Heise gauge graduated in 0.5 psi increments up to 85 atm. The gauge had a guaranteed accuracy of 0.1 percent of full scale. Its calibration was checked using an Ashcroft type 1327 portable deadweight tester. Temperatures were measured using a copper-constantan thermocouple and a digital thermocouple meter calibrated against known temperatures. Refrigeration was provided with a Harris industrial freezer. Control of the bomb temperature to within 0.1°C was accomplished using a fan, heater, and Thermistemp temperature controller. All valves were teflon packed and rated for high pressure use.

Methanol used was Fisher Spectranalyzed (R) with a stated purity of 99.95 percent. It was checked for water content using a gas chromatograph and dried when necessary with 3A molecular sieves to less than 0.05 percent water. Coleman grade carbon dioxide with a stated purity of 99.99 percent and ultra pure carrier grade nitrogen with a stated purity of 99.999 percent supplied by Air Products and Chemicals were used. A mixture of 1.5 percent hydrogen sulfide in nitrogen supplied by Linde Division of the Union Carbide Corporation was used.

Analysis of the samples was done on a Tracor Model 550 gas chromatograph equipped with a thermal conductivity cell, temperature programmer and heated gas sampling valve. A 3 meter long by 0.0032 meter diameter column packed with Porapak QS was used to achieve the separations. Compositions were determined using Southern Analytical's Supegrator 3 digital integrator and a Leeds and Northrop strip chart recorder. For the methanol-carbon dioxide system, the chromatograph was calibrated by mixing the components at below atmospheric pressures in the 10-ℓ vessel shown in Figure 9. Concentrations were determined from pressure measurements. For the multicomponent system, calibrations were done by injection of known amounts of each component.

Figure 8. Experimental Equipment.

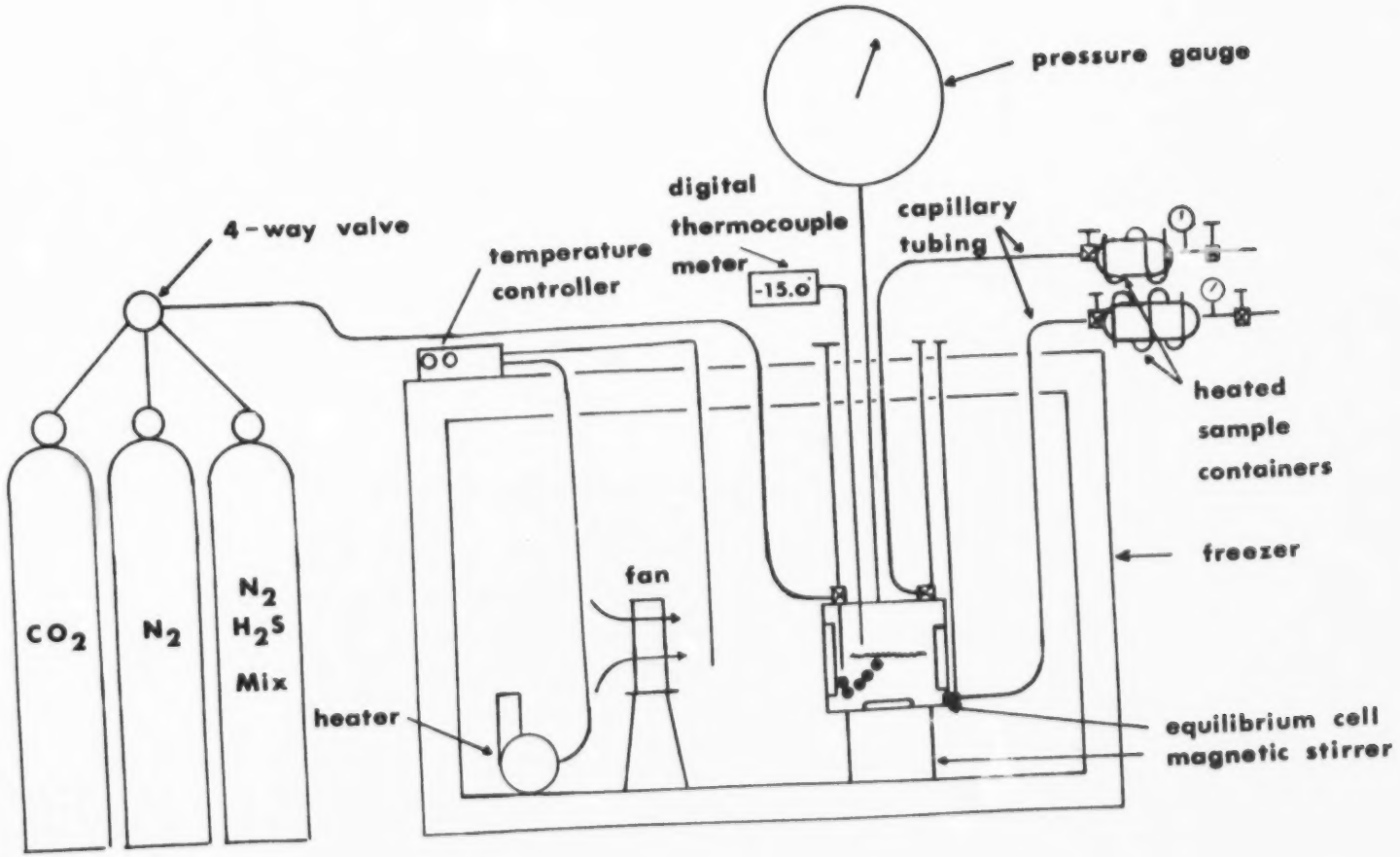
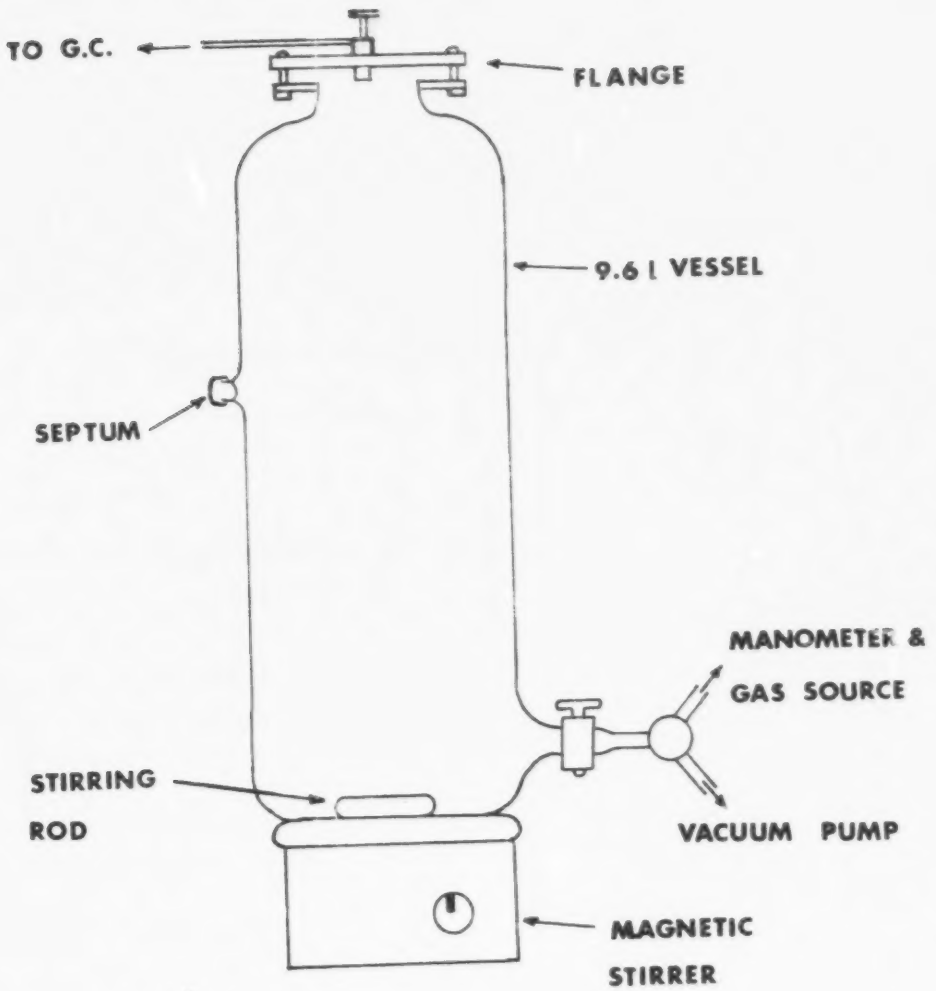


Figure 9. Calibration apparatus.



Before each series of runs, the equilibrium cell was filled with approximately 250-ml of methanol and then purged until no air or water could be detected leaving the cell. The cell was then pressurized and brought to the desired temperature. The gases of interest were added to achieve the desired pressure. The contents were agitated for at least six hours and then allowed to sit unagitated for at least twelve hours prior to sampling. Samples were allowed to expand through the capillary tubing into the evacuated sample containers. Sampling was done quickly and the cell pressure was seldom disturbed by more than 0.14 atm. The vapor sample container was pressurized to approximately 1.4 atm with helium and then both containers were heated to 140°C for five hours. The pressures in the containers were monitored to insure that they did not approach the vapor pressure of methanol. The contents of each container were analyzed a minimum of three times using the gas chromatograph.

SECTION 5

EXPERIMENTAL RESULTS

Methanol-Carbon Dioxide

For the purpose of verifying the proposed experimental procedure, vapor liquid equilibrium data were obtained for the carbon dioxide-methanol system. The data are compared with those of Yorizane et al. (4) in Figure 10 and to the model predictions in Table 22. From Figure 10, it is evident that the liquid phase concentration and pressure measurements show good agreement with those of Yorizane et al. (4). Table 22 shows the average percent deviation between calculated and experimental pressures to be 8.8, which is identical to that calculated from Yorizane's data. The vapor phase concentration of methanol is higher than expected and shows significant scatter. It is believed that liquid methanol became entrained with the vapor leaving the equilibrium cell during sampling. In these experiments pressures were measured to within 0.3 atm., temperatures within 0.1°C and compositions within 2 percent. These binary carbon dioxide-methanol vapor-liquid equilibrium data demonstrate the utility of the equipment and experimental procedure in obtaining and analyzing liquid samples. Using the present vapor sampling procedure unusually high and unpredictable concentrations of methanol can be expected in the vapor phase. Further experiments should be conducted in an apparatus modified to improve vapor sampling. At temperatures less than or equal to -15°C and at pressures greater than approximately 10 atm., the assumption that the vapor is methanol free introduces an error of less than 1 percent. If this sampling technique does not appreciably affect equilibrium, the equipment can be used to obtain data for a multicomponent system to serve as a check of the thermodynamic model.

Figure 10. P-x Diagram Experimental $CH_3OH(1)$-$CO_2(2)$ Data.

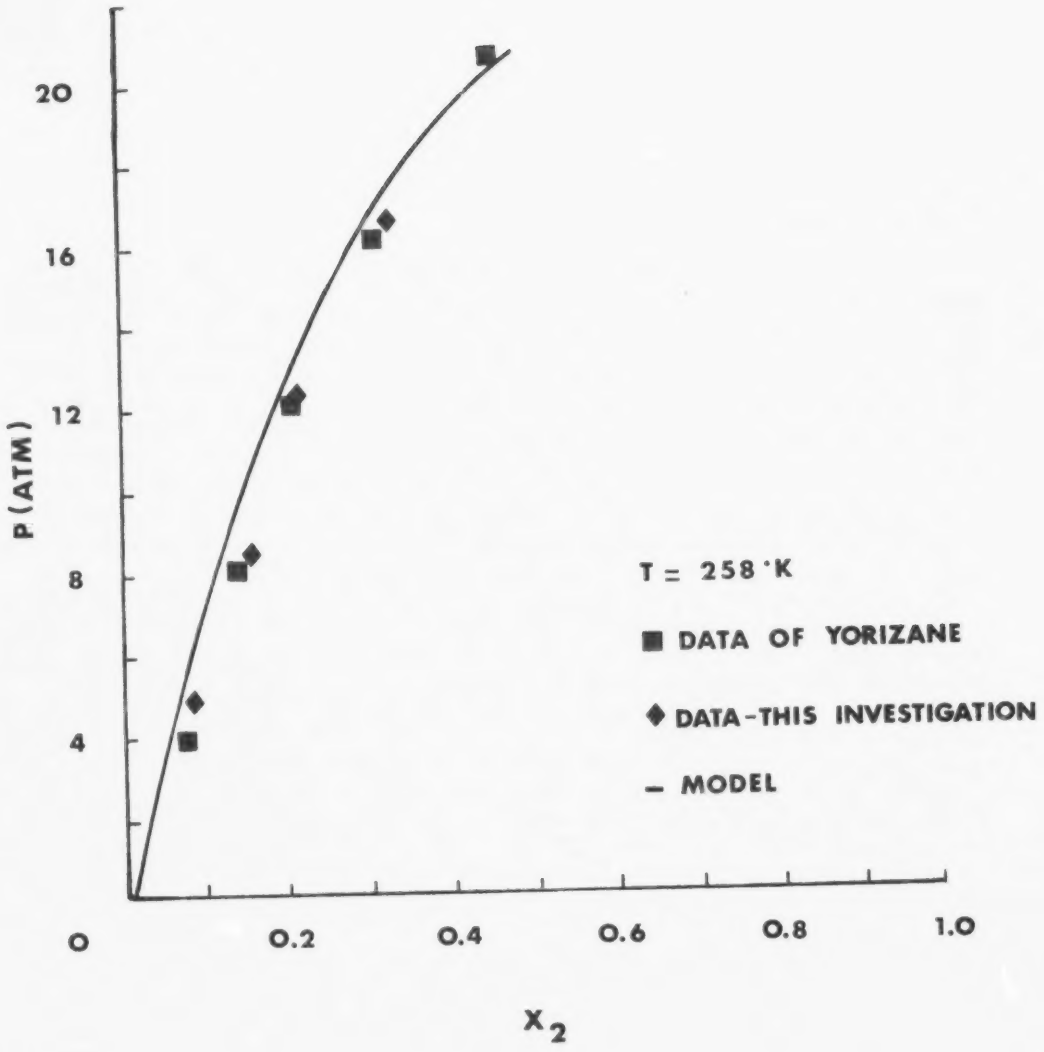


Table 22. Comparison of model and experimental equilibrium data for carbon dioxide-methanol at 258°K.

x_2	P_{exp} (atm)	P_{calc} (atm)	DP (atm)	$y_{2_{exp}}$	$y_{2_{calc}}$	Dy
0.085	5.03	5.76	0.73	0.936	0.997	0.061
0.149	8.45	9.24	0.79	0.995	0.998	0.003
0.227	12.13	12.84	0.71	0.980	0.999	0.019
0.349	16.30	17.21	0.91	0.912	0.999	0.087

Average percent deviation: in P, 8.8; in y, 4.6.

Multicomponent Equilibrium Data

Experimental equilibrium data were obtained for CO_2-H_2S-N_2-methanol mixtures at -15°C. These data are presented in Table 23. Precision of the analytical equipment varied among the system components: mole fractions of the most concentrated component could be determined to 1.5%; N_2 and CO_2 in the liquid could be determined to 2% and 8%, respectively; methanol and CO_2 in the vapor to within 2% and 1%, respectively. Confidence in hydrogen sulfide compositions was good at high pressures, but at low pressures a decrease in sensitivity of the thermal conductivity detector caused H_2S determinations to become less precise.

Equilibrium temperature and liquid composition were used with the algorithm BULP (described by Bass (30) to calculate system pressure and gas composition at equilibrium. Comparisons between calculated and experimental results are given in Table 24. The average deviation between calculated and experimentally measured pressures is 10.8%. Considerable differences between experimental and calculated gas compositions may also be noted. In general, pressure predictions are more accurate at low pressures while vapor composition predictions are more accurate at high pressures. The average percent deviation in pressure is only slightly worse than the 6.6 percent value calculated for all binaries used in determining and checking the model parameters. However, the percent deviation in vapor compositions is much worse. While not conclusive, it is believed that this unusually large discrepancy is due to ternary effects among the components carbon dioxide, hydrogen sulfide and methanol. Calculations made ignoring ternary effects show vapor compositions for carbon dioxide and hydrogen sulfide to be larger than the experimental values. Thus, gas cleanup systems will likely be overdesigned if calculations are based on vapor-liquid equilibrium predictions made by considering only binary interactions.

Table 23. Experimental vapor-liquid equilibrium data for methanol-carbon dioxide-nitrogen-hydrogen sulfide at -15.0°C.

P(atm)	x_{CH_3OH}	x_{CO_2}	x_{N_2}	x_{H_2S}	y_{CH_3OH}	y_{CO_2}	y_{N_2}	y_{H_2S}
8.23	0.945	0.052	0.002	0.001	0.003	0.319	0.677	0.001
9.37	0.927	0.069	0.003	0.001	0.002	0.276	0.722	-
9.75	0.929	0.067	0.003	0.001	0.002	0.270	0.726	0.001
19.9	0.909	0.083	0.007	0.001	0.002	0.134	0.863	0.001
27.9	0.919	0.070	0.010	0.001	0	0.101	0.898	0.001
34.6	0.920	0.065	0.013	0.002	0	0.085	0.913	0.002

Table 24. Comparison of calculated and experimental pressures and gas compositions for CO_2 - H_2S - N_2 - methanol

P(atm)			y_{CH_3OH}			y_{CO_2}			y_{N_2}			y_{H_2S}		
exp	calc	DP	exp	calc	Dy	exp	calc	Dy	exp	calc	Dy	exp	calc	Dy
8.23	7.77	0.46	0.003	0.002	0.001	0.319	0.493	-0.174	0.677	0.502	0.174	0.001	0.004	-0.003
9.37	10.77	-1.40	0.002	0.002	0	0.276	0.466	-0.190	0.722	0.053	0.192	-	0.003	-
9.75	10.66	-0.91	0.002	0.002	0	0.270	0.459	-0.189	0.726	0.537	0.189	0.001	0.003	-0.002
19.9	19.1	0.8	0.002	0.001	0.001	0.134	0.327	-0.193	0.863	0.863	0.192	0.001	0.002	-0.001
27.9	23.8	4.1	0	0.001	-0.001	0.101	0.234	-0.133	0.898	0.898	0.134	0.001	0.001	0
34.6	28.8	5.8	0	0.001	-0.001	0.085	0.188	-0.103	0.913	0.913	0.103	0.002	0.002	0

SECTION 6

SUMMARY OF RESULTS

1. A thermodynamic model was developed which successfully correlated binary vapor-liquid equilibrium data for the methanol-hydrogen sulfide, methanol-carbon dioxide, carbon dioxide-hydrogen sulfide and nitrogen hydrogen sulfide systems. The lack of adequate data prevented an adequate correlation for the methanol-nitrogen and carbon dioxide-nitrogen systems.

2. Experimental vapor-liquid equilibrium data were obtained for the methanol-carbon dioxide system at -15.0°C which showed excellent agreement in pressure and liquid phase composition measurements to literature data. Vapor compositions were unusually high in methanol.

3. Vapor phase composition and total pressure predictions made using the thermodynamic model showed poor agreement with experimental results. Predicted vapor compositions for carbon dioxide and hydrogen sulfide were larger than the experimental values. It is postulated that this is the result of ternary effects among this system components.

4. Models that do not require experimental data on ternary effects should be tested.

5. Additional modifications to the experimental equilibrium cell are needed to improve the vapor sampling technique.

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NOMENCLATURE

DP	=	$P_{calc} - P_{exp}$
Dy	=	$y_{calc} - y_{exp}$
f_i	=	fugacity of i
f_i°	=	fugacity of i in reference state
H_i	=	Henry's constant for i
k_{ij}	=	binary constant, Equation 9f
n_i	=	moles of i
P	=	pressure
P_r	=	reduced pressure
P_{c_i}	=	critical pressure of i
P_i^*	=	vapor pressure of i
R	=	gas constant
T	=	temperature
T_r	=	reduced temperature
v	=	molar volume
V_c	=	critical volume
V_i^L	=	liquid molar volume of i
y_i	=	mole fraction i in gas phase

Greek Symbols

γ_i	=	activity coefficient of i
ϕ_i	=	fugacity coefficient of i
ϕ_i^*	=	fugacity coefficient of saturated i
ω	=	Pitzer accentric factor
$\Omega_{a_i}, \Omega_{b_i}$	=	dimensionless pure component constants, Table 6